

# Controlling the Interactions between Soft Colloids via Surface Adsorption

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## Abstract

By employing monomer-resolved computer simulations and analytical considerations based on polymer scaling theory, we analyze the conformations and interactions of multiarm star polymers strongly adsorbed on a smooth, two-dimensional plane. We find a stronger stretching of the arms as well as a stronger repulsive, effective interaction than in the three dimensional case. In particular, the star size scales with the number of arms  $f$  as  $\sim f^{1/4}$  and the

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effective interaction as  $\sim f^2$ , as opposed to  $\sim f^{1/5}$  and  $\sim f^{3/2}$ , respectively, in three dimensions. Our results demonstrate the dramatic effect that geometric confinement can have on the effective interactions and the subsequent correlations of soft colloids in general, for which the conformation can be altered as a result of geometrical constraints imposed on them.

# Introduction

Physical confinement of complex fluids in small pores, films, or tubes is known to induce significant changes in their structural and dynamical properties and phase behavior, including the emergence of surface-related phase transitions<sup>1,2</sup> the modification of bulk critical phenomena,<sup>3,4</sup> novel types of ordering<sup>5–11</sup> as well as a shifting of dynamical arrest lines.<sup>12</sup> As such, the detailed microscopic understanding of this confinement-based phenomenology is of great importance both scientifically and technologically. Already when hard, nondeformable colloids are restricted within a slit<sup>5,6</sup> or on the interface between two immiscible fluids,<sup>7,9</sup> important new mechanisms come forward which affect the effective interactions between the constituent particles. Common examples are the softening of the interactions emerging from averaging-out the transversal degrees of freedom<sup>6,13</sup> or the development of strong electric dipoles due to dielectric mismatch between the immiscible fluids forming the interface.<sup>9,10</sup> To date, substantial progress has been made, both experimentally and theoretically, towards the understanding of the behavior of hard-sphere-like fluids<sup>11</sup> as well as of dipolar mixtures under confinement.<sup>7,9</sup>

Confined systems comprised of soft particles have received substantially less attention.<sup>8,14</sup> Even in the cases in which soft potentials have been considered, a simplifying assumption has been made, namely that the confined entities are point particles whose interaction potential does not depend on geometric confinement. However, for a wide class of common soft particles, ranging from polymer brushes to dendrimers and from microemulsions to microgels, the confining walls *physically* deform the particle, resulting into conformational changes that affect their interaction in substantial ways. No attempt has been undertaken to-date to take this important aspect into account and to then proceed towards an investigation of the structure of soft, deformable particles in the borderline between two and three dimensions. At the same time, soft systems possess important unique properties due to their inherent tunability. Thus, the effective interaction potential between two star polymers is known to change significantly in going from bulk (three dimensions) to planar confinement (two dimensions).<sup>15</sup> Therefore, this tunability presents both advantages and additional challenges.

The central goal of the present work is to study structural properties of star polymers under confinement, where the confined conditions are created through adsorption of the star polymers on a planar wall, with the degree of confinement controlled via the star-wall adsorption strength. The behavior of star polymers in the vicinity of a substrate is important for a variety of scientific and technological applications. For example, formation of colloidal aggregates with desired ordered structure on a substrate can be achieved by controlling effective colloidal interactions via the use of star polymers which act as depletants. As such, adsorption of star polymers has been actively studied both experimentally<sup>16,17</sup> and theoretically.<sup>18–24</sup>

The present study is motivated by the recent work that has demonstrated a dramatic amplification of tension along the backbone of branched macromolecules as a result of their adsorption on a substrate.<sup>25–28</sup> By analogy, one would expect that adsorption on a surface would result in an enhancement of repulsive interaction between the two star polymers.<sup>15</sup> In the work at hand, this conjecture is confirmed and quantified both via Molecular Dynamics (MD) simulations and scaling theoretical calculations. In particular, based on scaling arguments, we propose a simple and accurate functional form for describing mean force between two adsorbed stars, which is found to be in excellent agreement with the simulation results for all the combinations of parameter values studied.

## Computational model

We consider a three-dimensional coarse-grained model<sup>29</sup> of a polymer star which consists of  $f$  linear arms with one end free and the other one tethered to a microscopic core (seed monomer) of size  $R_c$ , which is of the order of the monomer size  $\sigma$ . Each arm is composed of  $N$  particles of equal size and mass, connected by bonds. Thus, the total number of monomers in the star (excluding the core) is  $fN$ . Previous studies on star polymers<sup>30</sup> has shown that this model capture all the characteristics of the stars' conformations and interactions. The bonded interaction between subsequent beads is described by frequently used Kremer-Grest model<sup>31</sup>  $V^{\text{KG}}(r) = V^{\text{FENE}}(r) + V^{\text{WCA}}(r)$ , with the

so-called 'finitely-extensible nonlinear elastic' (FENE) potential:

$$V^{\text{FENE}}(r) = -0.5kr_0^2 \ln[1 - (r/r_0)^2]. \quad (1)$$

The non-bonded interactions between monomers are taken into account by means of the Weeks-Chandler-Anderson (WCA) interaction, i.e., the shifted and truncated repulsive branch of the Lennard-Jones potential, given by:

$$V^{\text{WCA}}(r) = 4\epsilon \left[ (\sigma/r)^{12} - (\sigma/r)^6 + 1/4 \right] \theta(2^{1/6}\sigma - r). \quad (2)$$

In Eqs. (??) and (??),  $r$  denotes the distance between the centers of two monomers (beads), while the energy scale  $\epsilon$  and the length scale  $\sigma$  are chosen as the units of energy and length, respectively. Accordingly, the remaining parameters are fixed at the values  $k = 30\epsilon/\sigma^2$  and  $r_0 = 1.5$ . In Eq. (??) we have introduced the Heaviside step function  $\theta(x) = 0$  or  $1$  for  $x < 0$  or  $x \geq 0$ . In consequence, the steric interactions in our model correspond to good solvent conditions. The substrate in the present investigation is considered simply as a structureless adsorbing plane, with a Lennard-Jones potential acting with strength  $\epsilon_s$  in the perpendicular  $z$ -direction,  $V^\perp(z) = 4\epsilon_s[(\sigma/z)^{12} - (\sigma/z)^6]$ . Since in the the majority of our simulations we considered the case of *strong* adsorption,  $\epsilon_s/(k_B T) = 5$  with  $k_B = 1$  and  $T = 0.12\epsilon/k_B$ , the configurations of the simulated stars were two-dimensional. The chosen value  $\epsilon_s$  resulting into an adsorption energy of  $5k_B T$  corresponds to values in the typical experimental range.<sup>32</sup> For comparison and completeness, we have also examined the case of stars confined between two parallel, repulsive walls (slit). In this case, stars form quasi two-dimensional configurations, since small lateral excursions of the order of the slit width  $H$  are allowed. The wall-monomer was modeled by WCA-potentials given by Eq. ?? acting only in  $z$ -direction and the slit width was set to  $H = 4\sigma$ .

The equilibrium dynamics of the chains is obtained by solving the Langevin equation of motion

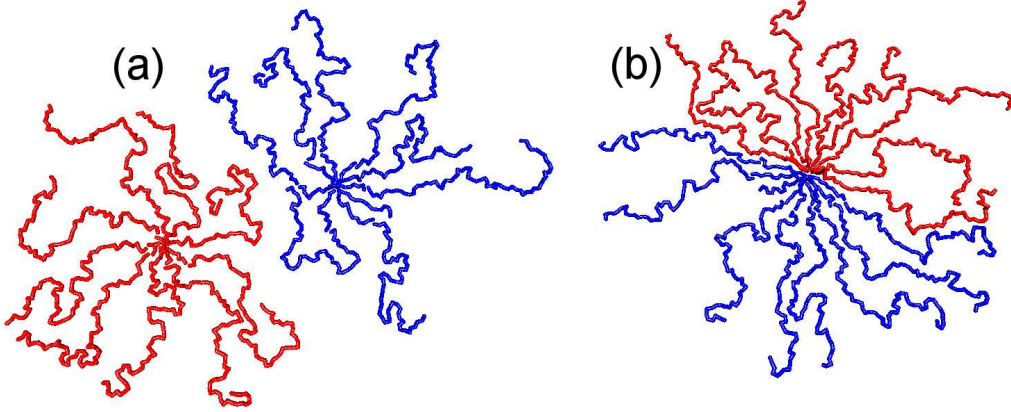


Figure 1: Snapshots of thermalized star-polymers with  $f = 9$  and  $N = 75$  adsorbed on a solid substrate displayed for different separation distances: (a)  $d = 35\sigma$ ; (b)  $d = 3\sigma$ .

for the position  $\mathbf{r}_n = [x_n, y_n, z_n]$  of each bead in the star,

$$m\ddot{\mathbf{r}}_n = \mathbf{F}_n^{\text{FENE}} + \mathbf{F}_n^{\text{WCA}} - \zeta\dot{\mathbf{r}}_n + \mathbf{R}_n(t), \quad n = 1, \dots, fN \quad (3)$$

which describes the Brownian motion of a set of interacting monomers. Even though Molecular Dynamics would be equally well-suited for gathering equilibrium statistics, the approach based on the Langevin equation allows for the introduction of a fixed temperature via the coupling to a random force (see below) in a natural way. In Eq. (??) above,  $\mathbf{F}_n^{\text{FENE}}$  and  $\mathbf{F}_n^{\text{WCA}}$  are the deterministic forces exerted on monomer  $n$  by the remaining bonded and nonbonded monomers, respectively. The influence of the solvent is split into a slowly evolving viscous force  $-\zeta\dot{\mathbf{r}}_n$  and a rapidly fluctuating stochastic force. This random, Gaussian force  $\mathbf{R}_n$  is related to friction coefficient  $\zeta$  by the fluctuation-dissipation theorem. The integration step employed was  $\Delta t = 0.002$  time units, whereby time is measured in units of  $\sqrt{m\sigma^2/\varepsilon}$ ,  $m = 1$  denoting the mass of the beads. The ratio of the inertial forces over the friction forces in Eq. (??) is characterized by the Reynolds number  $\text{Re} = \sqrt{m\varepsilon}/\zeta\sigma$  which in our setup is  $\text{Re} = 4$ . In the course of simulation the velocity-Verlet algorithm was employed to integrate the equations of motion (??).

Starting configurations were generated as radially straight chains fixed to the immobile seed monomers. Stars were placed at a distance  $z = \sigma$  above the surface and at large separation dis-

tance between seeds  $d$ , in order to avoid monomer overlaps between neighboring molecules. As a next step star-polymers were equilibrated until they adopted their equilibrium configurations, from which sizes and monomer profiles have been determined. The required equilibration time depend on  $f$  and  $N$ , i.e.,  $5 \times 10^5$  time steps for the smallest stars and up to  $2 \times 10^6$  for the largest. As a next step star-polymers were equilibrated until they adopted their equilibrium configurations. This step was controlled by monitoring the time evolution of the center-to-end radius  $R_e$  and the gyration radius  $R_g$ , as well as of the and radial density profiles of the stars.

Well-equilibrated configurations from a large interstar separation were used as starting points for the next simulation, for which we move the second seed by distance  $\Delta d$  closer to the first one and repeated the equilibration step. In order to sample the interaction force for each equilibrated configuration (at a given distance  $d$ ) a production run was performed during which time averaged force  $\langle F(t, d) \rangle = F(d)$  exerted on the seed was computed. To assure that our measured forces were true equilibrium results, we have also employed the reverse path of first bringing the two seeds very close to one another and then increasing their mutual distance. The resulting force vs.-distance curves turned out to be independent of the procedure of moving the stars close or away from each other, excluding thus any hysteresis effects in our simulations.

During the force measurement all particles (including the cores of the stars) were allowed to fluctuate in the  $z$ -direction. The fluctuations of seeded monomers in the  $z$ -direction do not contribute to the mean force  $F(d)$ , since the time average of the  $z$ -component of the force,  $\langle F_z(t, d) \rangle$ , for seeded monomers vanishes. The run was continued until the uncertainty of the average forces for all three components dropped below  $0.005\epsilon/\sigma$ . Our checks have also shown that time averaged net force acting on the seed is equivalent to the time averaged force felt by the core of a star polymer. Typical simulation snapshots of two interacting stars are presented in 1.

## Theory and comparison with simulations

The theoretical approach we adopt for describing both single-star conformational properties and the effective interaction between two strongly adsorbed stars is based on the Daoud-Cotton blob picture<sup>33</sup> of multiarm stars and its generalization to two interacting stars,<sup>34</sup> appropriately adopted to two spatial dimensions. Each of the  $f$  arms around the center of a star can be considered as being built of a succession of concentric blobs of radius  $\xi(s)$ , where  $s$  denotes the distance from the star center. The polymer segment confined within each blob is performing a two-dimensional, self-avoiding random walk (SARW), whereas the blobs are space-filling within the star corona. The latter assumption leads to the scaling  $\xi(s) \cong s/f$ ; the former implies that the number of monomers,  $g(s)$ , from a single chain at distance  $s$  from the center, scale as  $g(s) \sim \xi^{1/\nu}(s)$ , where  $\nu = 3/4$  is the SARW-critical exponent in two dimensions. Concomitantly, the monomer concentration  $c(s)$  scales with the distance from the star center as:

$$c(s) \simeq \frac{f \xi^{1/\nu}(s)}{2\pi s \xi(s)} \sim f^{2-1/\nu} s^{1/\nu-2} a^{-1/\nu}, \quad (4)$$

where  $a$  denotes the segment size. Using the value of the scaling exponent  $\nu=3/4$  in two dimensions under good solvent conditions,<sup>15</sup> one obtains:

$$c(s) \simeq f^{2/3} \left(\frac{a}{s}\right)^{2/3} a^{-2}. \quad (5)$$

The size of the star  $R$ , standing for, e.g., its gyration radius  $R_g$  or its center-to-end radius  $R_e$ , can be determined by the conservation law of the monomer number,  $fN = 2\pi \int_0^R c(s) s ds$ . The scaling of  $R$  follows:

$$R \sim a f^{1/4} N^{3/4}, \quad (6)$$

featuring a stronger stretching effect of the arms with  $f$  in comparison to the three-dimensional case,<sup>33</sup> in which  $R \sim a f^{1/5} N^{3/5}$ . The above relations for  $c(s)$  and  $R$  imply that the scaled monomer



concentration  $R^2 c(s)/(Nf)$  is a universal function  $\rho(x)$  of  $x \equiv r/R$ , with the properties:

$$2\pi \int_0^1 \rho(x) x dx = 1 \quad \text{and} \quad \rho(x) \sim x^{-2/3} \text{ for } x \leq 1. \quad (7)$$

Our MD simulation results in 2 fully confirm this picture, since density profiles from three different stars collapse onto one another when properly scaled, showing in addition the power-law predicted by Eq. (??). Furthermore, the validity of Eq. (??) is demonstrated in 3, where the quantity  $f^{-1/4} R_g$  is shown to indeed scale as  $N^{3/4}$ . Scaling- and blob-based considerations are thus fully capable of predicting quantitatively the properties of strongly adsorbed, individual star polymers.

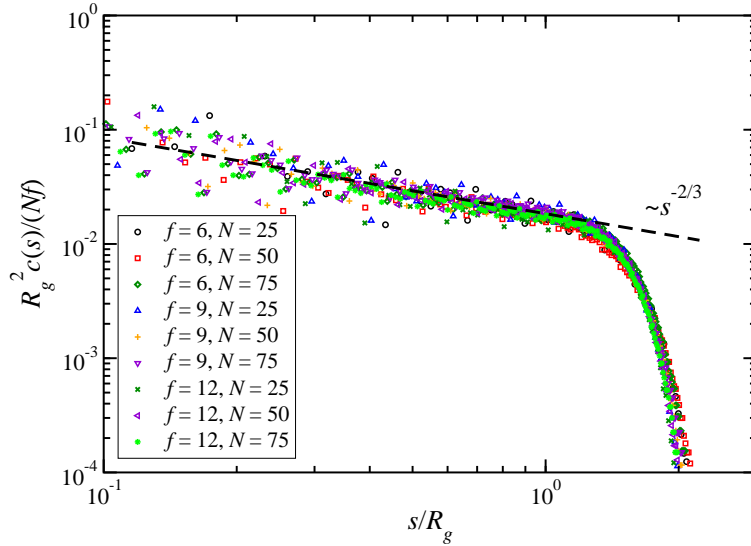


Figure 2: MD simulation results for the normalized monomer density profiles for various star polymers as a function of dimensionless distance from the star center; the dashed line indicates the predicted power-law,  $c(s) \sim s^{-2/3}$ .

The theoretical approach to the functional form of the effective interaction  $\beta V_{\text{eff}}(d)$  between two star polymers in two dimensions, whose anchoring points are separated by distance  $d$ , proceeds along two parallel lines, one pertaining to the case  $f = 1$  (two polymer chains) and the second to the case  $f \gg 1$  (multiarm stars). For  $f = 1$ , we consider first the case of a single, self-avoiding chain of  $N$  segments, which possesses a partition function  $Z_1(N)$  that scales as  $Z_1(N) \sim \tau^N N^{\gamma-1}$ .<sup>34</sup> Here,  $\tau$  is a model-dependent parameter and  $\gamma = 43/32$  is another universal exponent of the 2d-SARW.<sup>15</sup>

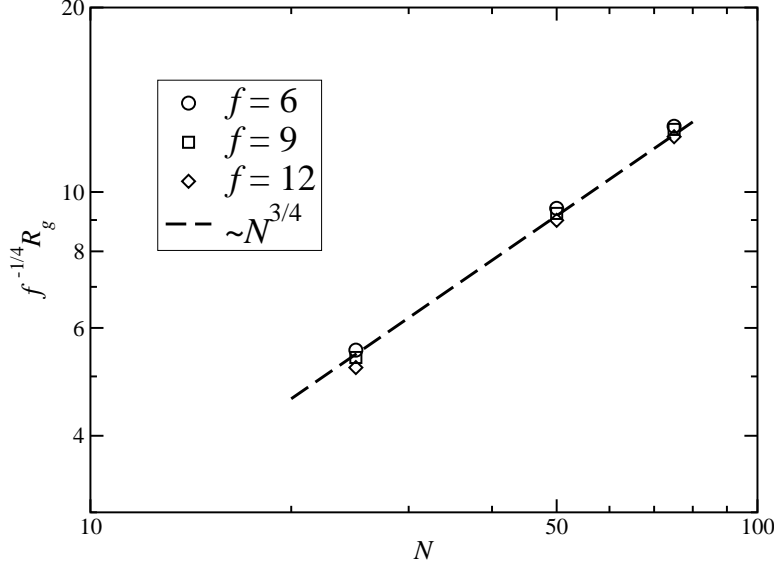


Figure 3: Simulation results for the star radius  $R_g$  scaled by  $f^{1/4}$  as a function of the star arm length  $N$  for several values of  $f$  and  $N$ ; the dashed line indicates the power law of Eq. (??).

Two such stars, when kept at infinite separation, are thus characterized by a partition function  $Z_2(d \rightarrow \infty) = Z_1^2(N) \sim \tau^{2N} N^{2(\gamma-1)}$ . When their end-monomers are kept at separation  $r \sim a$ , the two chains resemble a single SARW of  $2N$  steps, thus  $Z_2(d \sim a) \sim \tau^{2N} (2N)^{\gamma-1}$ . On the other hand, the segment length can be renormalized to larger values as long as it does not exceed, roughly, the equilibrium chain size  $R$ . The effective interaction is given as  $\beta V_{\text{eff}}(d) = -\ln[Z_2(d)/Z_2(d \rightarrow \infty)]$ . Using the above considerations in conjunction with the relation  $R \sim N^\nu$ , we obtain

$$\beta V_{\text{eff}}(d) = -\frac{\gamma-1}{\nu} \ln\left(\frac{d}{R}\right) \text{ for } d \lesssim R, \quad (8)$$

for the case  $f = 1$ , where  $(\gamma-1)/\nu = 11/24$ .

In the opposite case,  $f \gg 1$ , we proceed by first counting the number of Daoud-Cotton blobs,  $M(f)$ , of a single star. The condition  $c(s) \sim \xi^{1/\nu}(s)$  together with the geometrical picture of closely-packed blobs lead, after some straightforward algebra, to the result  $M(f) \sim f^2 \ln(R/R_c)$ , where  $R_c$  is a (microscopic) scale denoting the size of the core of the star, on which the chains are grafted; this result should be compared with the corresponding scaling  $M(f) \sim f^{3/2} \ln(R/R_c)$  in three dimensions,<sup>34</sup> demonstrating, once more, the stronger stretching of the chains in two

dimensions. If two such multiarm stars are now brought to a separation of order  $R_c$  from one another, they resemble a single star with  $2f$ -arms, forming a number  $M(2f) \sim (2f)^2 \ln(R/R_c)$  blobs. The effective interaction can be estimated by assigning the usual free energy cost of  $k_B T$  per blob, i.e.,  $\beta V_{\text{eff}}(d) \sim M(2f) - 2M(f)$ , leading to the expression:

$$\beta V_{\text{eff}}(d) = -\Theta(f) \ln \left( \frac{d}{R} \right) \text{ for } d \lesssim R, \quad (9)$$

where the amplitude scales as  $\Theta(f) \sim f^2$  for  $f \gg 1$ .

Since a single chain ( $f = 1$ ) can be seen as a special case of a star polymer and the short-range behavior of the effective potential is logarithmic with  $r$  in both cases, it is reasonable to request that  $\Theta(f = 1) = 11/24$  and introduce a general expression for this amplitude that smoothly interpolates between the two extreme cases. Field-theoretical arguments lead to the expression:<sup>15</sup>

$$\Theta(f) = \frac{2 + 9f^2}{24}, \quad (10)$$

which, evidently, satisfies the requirements on both limits,  $f \rightarrow 1$  and  $f \gg 1$ . The ultrasoft logarithmic repulsion for the star-star interaction potential has been obtained earlier *in three dimensions* on a similar basis, with the corresponding short-range repulsive force behaving as  $(5f^{3/2}/18) \ln(R/d)$ .<sup>35</sup> The functional form of the short range star-star interaction remains the same but its amplitude increases due to confinement from  $5f^{3/2}/18$  to  $(2 + 9f^2)/24$ .<sup>15</sup>

The effective force  $F_{\text{short}}(d)$  for  $d \lesssim R$  follows as minus the gradient of  $V_{\text{eff}}(d)$ . Taking into account that for  $d \rightarrow R_c$  the strong steric interaction between the cores dominates over the universal, logarithmic form of the latter arising from polymer self-avoidance, we are led to introduce a shift  $d \rightarrow d - R_c$  on the coordinate, as previously done also for three-dimensional star polymers,<sup>30</sup> yielding:

$$\frac{F_{\text{short}}(d)}{k_B T} = \frac{2 + 9f^2}{24(d - R_c)}. \quad (11)$$

In the long-range regime, Flory theory yields a Gaussian form for the potential of mean force,

which results into the following scaling expression for the mean force at long ( $d > R_e$ ) star-star separations:<sup>36</sup>

$$\frac{F_{\text{long}}(d)}{k_B T} = \frac{2 + 9f^2}{24(R_e - R_c)} \frac{d}{R_e} \exp \left[ - (d/R_e)^2 \right]. \quad (12)$$

Here, the prefactor has been determined using the physical requirement of continuity between the short- and long-range forces at  $d = R_e$ . The corresponding results for the mean force between two adsorbed stars are shown in 4 together with the simulation data for several values of  $f$  and  $N$ ; the agreement between theory and simulation is excellent for all values of parameters studied, without use of fit parameters.

Setting  $x \equiv d/R_e$  and taking the limit  $R_c \rightarrow 0$  (long chains), we put forward a simple and accurate analytical form for the effective potential between two star polymers in two dimensions as:

$$\beta V_{\text{eff}}(x) = \frac{2 + 9f^2}{24} \begin{cases} -\ln x + e^{-1}/2, & \text{if } x \leq 1, \\ e^{-x^2}/2, & \text{if } x > 1. \end{cases} \quad (13)$$

Eq. (??) extends the hitherto known three-dimensional result<sup>35</sup> to two dimensions, introducing an easy to handle functional form for the latter. The ultrasoft potential of a logarithmic form is a universal feature also for the interaction of dissimilar star polymers<sup>37</sup> or between star polymers and flat or curved walls<sup>38</sup> in three dimensions. The criterion of a ‘weak mean field fluid’,<sup>39</sup> expressed through the condition  $\hat{V} \equiv \int_0^\infty x^{d-1} V_{\text{eff}}(x) dx < \infty$ , is fulfilled for the effective interaction of Eq. (??).

Finally, in 5 we compare our simulation results for the two distinct cases already mentioned above: stars strongly adsorbed on a single wall and stars trapped between two parallel, repulsive walls forming a slit of width  $H = 4\sigma$  in the  $z$ -direction. The data indicate a systematic deviation of the two forces, with growing inter-star separation distance  $d$ . As long as the two stars are far apart in the slit, the arms on their periphery experience very low monomer density in their vicinity, and can easily slip above or beneath one another. This is reflected by the smaller force of repulsion, felt by the stars, compared to the case of strong adsorption. In the latter case, the arms cannot intersect

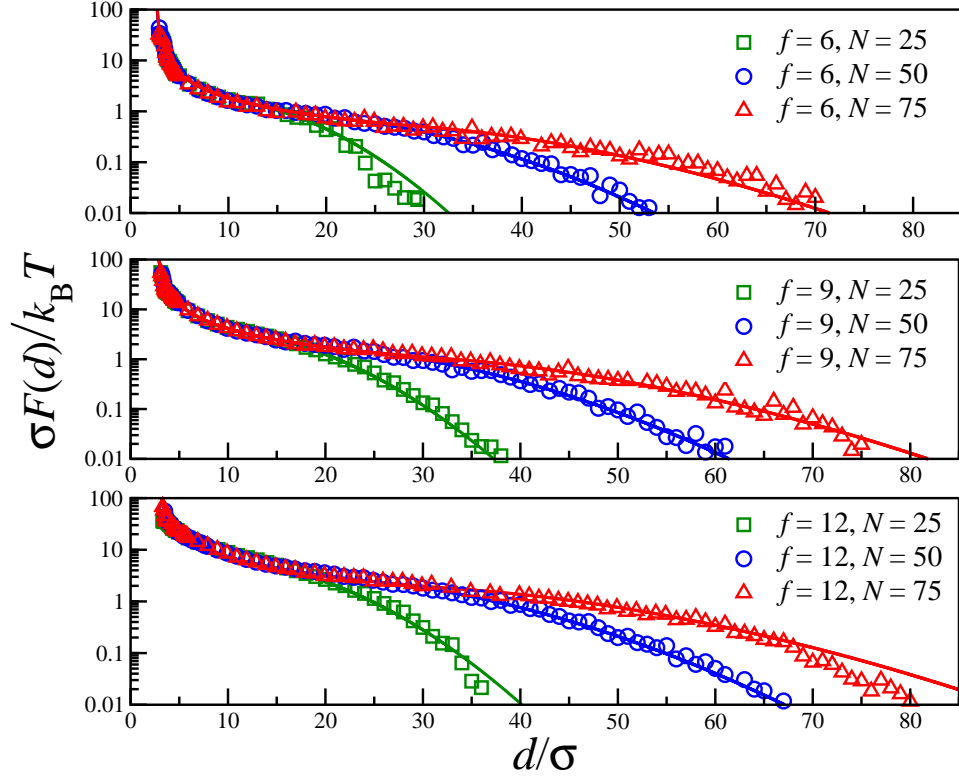


Figure 4: MD simulation (symbols) and scaling theory (lines) results for the mean force between two adsorbed stars for several values of  $f$  and  $N$ , as indicated in the legends.

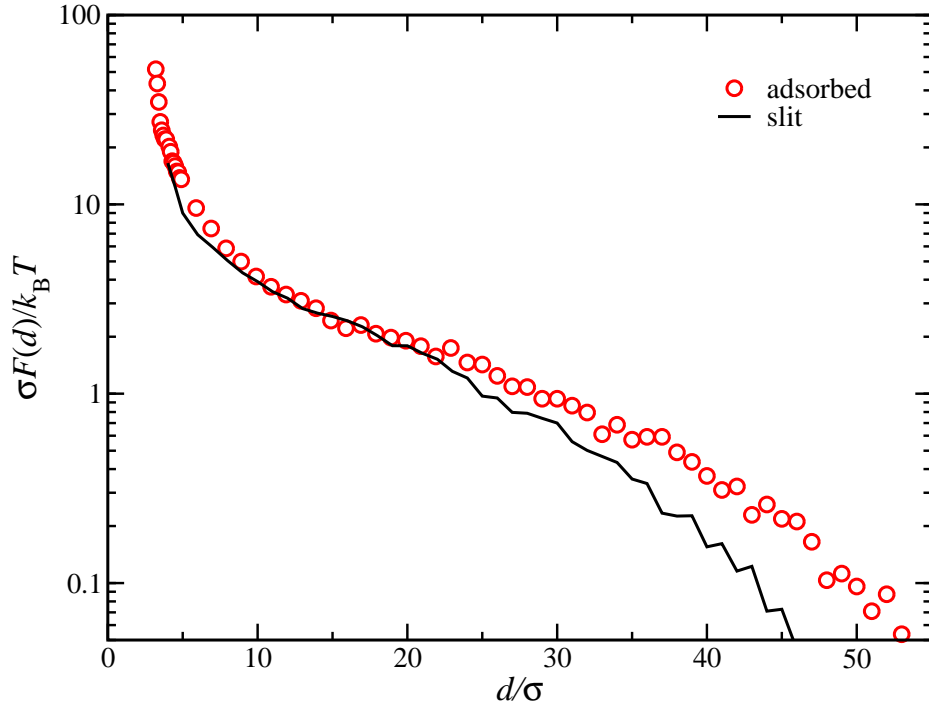


Figure 5: Comparison of MD simulation results for the mean force between two stars adsorbed onto surface (circles) or trapped in a slit (solid line). Here  $f = 9$  and  $N = 50$ . Slit width is  $4\sigma$ .

as they stick strongly to the substrate, so they either have to bend when encountering an arm of the second star (meaning stronger repulsion), or crawl over it which is less probable because it costs energy of contacts with the substrate. On the other hand, the forces coincide at smaller distances  $d$  because the increased density around the star centers largely prevents easy threading of arms through each other, so that there is no way to avoid the strong repulsion.

## Conclusion

We have demonstrated by a combination of molecular simulation and analytical theory that soft colloids, represented here by the common example of star polymers, experience dramatic conformational changes upon confinement in two dimensions, which profoundly affect their effective interaction, rendering it significantly more repulsive than in three dimensions. Previous studies on three-dimensional star polymers<sup>40</sup> indicated that the pair forces continue to provide a valid and accurate description of the interactions even for the case in which three stars approach each other at distances that represent a small fraction of their respective sizes. Thus, our results for effectively two-dimensional star polymers are expected to be quantitatively reliable for concentrations well above the overlap density of the stars. In addition our checks have shown that effective interaction between two adsorbed stars is the same as the effective force for stars trapped in a very narrow slit formed by two parallel and repulsive walls. Accordingly, we expect that much stronger ordering will take place in confinement and that the structural arrest lines will shift to lower concentrations with respect to their bulk values. Changing the amplitude of the attractive interaction to the wall allows us to tune the conformations and the interactions of the (partially) adsorbed stars, opening a pathway to tunable patterning of surfaces with ordered arrays of adsorbed stars.

Possible experimental validation of our theoretical predictions would be to graft long chains on colloidal particles and use optical tweezers in order to measure effective force. The alternative approach would be to measure the correlations between the adsorbed stars in the same way this has been done for other 2d-colloidal systems adsorbed on surfaces or interfaces (see e.g.<sup>41</sup>). The

resulting correlations should then be describable by the effective interactions derived in this paper.

Our work opens up a possibility to consider also the case of partially absorbed stars with  $f_a$  chains lying on the plain and  $f - f_a$  chains assuming 3d-configurations, for which the force can be obtained as the sum of the 2d- and 3d-expressions, each weighted with the appropriate amplitude. The determination of the interaction between partially adsorbed stars, bridging the gap between two and three dimensions, will be the subject for future work.

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